PATENT ABSTRACTS OF JAPAN

(11)Publication number:

2004-186061

(43) Date of publication of application: 02.07.2004

(51)Int.CI.

H01M 4/04 H01M 4/02

H01M 10/40

(21)Application number: 2002-353487 (22)Date of filing:

05.12.2002

(71)Applicant : NISSAN MOTOR CO LTD

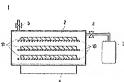
(72)Inventor: SENBOKUTANI RYOICHI

FUKUZAWA TATSUHIRO

(54) MANUFACTURING DEVICE OF LITHIUM ION SECONDARY BATTERY. MANUFACTURING METHOD OF LITHIUM ION SECONDARY BATTERY, LITHIUM ION SECONDARY BATTERY, BATTERY PACK CONSISTING OF LITHIUM ION SECONDARY BATTERY, AND CAR USING THIS BATTERY PACK

(57) Abstract:

PROBLEM TO BE SOLVED: To provide a manufacturing method of a lithium ion secondary battery in which active material density of an electrode is improved. SOLUTION: A current collector 10 coated by an electrode slurry 11 before polymerization is placed in a pressure vessel 2, and while the pressure vessel 2 is pressurized by an inert gas from a gas cylinder 3, the interior of the pressure vessel is overheated by a heater 6, electrode slurry 11 before the polymerization is polymerized, and an electrode is formed.



* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.*** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

(Claim 1)

A pressure vessel for laying in an inside a charge collector in which electrode material before a polymerization was applied.

A force means for pressurizing inside of said pressure vessel at specified pressure.

An energy supply means to supply energy required since electrode material before said polymerization polymerizes within said pressure vessel of said specified pressure,

A manufacturing installation of a ****(ing) lithium ion secondary battery.

[Claim 2]

Heating apparatus with which said energy supply means heats inside of said pressure vessel, an ultrasonic irradiation apparatus which irradiates electrode goods before said polymerization with an ultrasonic wave, A manufacturing installation of the lithium ion secondary battery according to claim 1 being either at least among black lights which irradiate electrode goods before said polymerization with ultraviolet rays.

[Claim 3]

A manufacturing installation of the bipolar battery according to claim 1 or 2, wherein said specified pressure is 0.5 - 10MPa.

[Claim 4]

A stage of laying a charge collector in which electrode material before a polymerization was applied in a pressure vessel,

A stage which pressurizes inside of said pressure vessel at specified pressure,

A stage which supplies energy required since electrode material before said polymerization polymerizes within said pressure vessel pressurized by said specified pressure,

A manufacturing method of a ****(ing) lithium ion secondary battery.

[Claim 5]

A stage which applies a positive pole substance before a polymerization to the 1st field of a charge collector,

A stage of laying said charge collector in which a positive pole substance before said polymerization was applied in a pressure vessel,

A stage which pressurizes inside of said pressure vessel at specified pressure,

A stage which supplies energy required since a positive pole substance before said polymerization polymerizes within said pressure vessel pressurized by said specified pressure,

A stage which applies a negative-electrode substance before a polymerization to the 2nd field of said charge collector,

A stage of laying said charge collector in which a negative-electrode substance before said polymerization was applied in said pressure vessel,

A stage which pressurizes inside of said pressure vessel at specified pressure,

A stage which supplies energy required since a negative-electrode substance before said polymerization polymerizes within said pressure vessel pressurized by said specified pressure, A manufacturing method of a ****(ing) lithium ion secondary battery.

[Claim 6]

Said positive pole substance contains positive active material which consists of a lithium transition metal multiple oxide.

A manufacturing method of the bipolar battery according to claim 5, wherein said negativeelectrode substance contains negative electrode active material which consists of carbon or a lithium transition metal multiple oxide.

[Claim 7]

A manufacturing method of the bipolar battery according to claim 5 or 6, wherein said specified pressure is 0.5 - 10MPa.

[Claim 8]

A lithium ion secondary battery laminating two or more charge collectors on both sides of an electrolyte between electrodes manufactured by a manufacturing method of a lithium ion secondary battery of any one description of the Claims 5-7.

[Claim 9]

A lithium ion secondary battery the feature and, wherein [to carry out / according to claim 8] said electrolyte is a solid polymer electrolyte.

[Claim 10]

A cell group connecting two or more lithium ion secondary batteries according to claim 8 or 9 in parallel and/or in series.

[Claim 11]

A car using the cell group according to claim 10 as a power supply of a motor for driving a wheel.

[Translation done.]

* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

This invention relates to the manufacturing installation of a lithium ion secondary battery, the manufacturing method of a lithium ion secondary battery, a lithium ion secondary battery, the cell group that consists of lithium ion secondary batteries, and the car using this cell group. [0002]

[Description of the Prior Art]

An electrode is formed in the at least 1 surface of a charge collector, and the cell of the structure laminated between this electrode as sandwiched the electrolyte is in a lithium ion secondary battery.

[0003]

After completing an electrode conventionally using the binder which consists of fluororesin material as a manufacturing method of the electrode section in the lithium ion secondary battery of such a structure, there is a method of dissolving a polymer electrolyte and impregnating with this binder (for example, refer to patent documents 1.).

[0004]

[Patent documents 1]

JP,2000-138073,A

[0005]

[Problem(s) to be Solved by the Invention]

However, there is a problem that the electrolyte used as an electrode active material cannot fully be filled up with the conventional manufacturing method in a binder. If this has little quantity of the solvent used when dissolving an electrolyte, for example, since viscosity becomes high, it will become a cause by which it does not fully spread in a binder but a filling factor becomes low. On the other hand, if there is much quantity of a solvent, after evaporating a solvent, the quantity of the electrolyte itself which remains in a binder will decrease, and an electrolytic fill ration will fall

too. [0006]

Then, in the lithium ion secondary battery of the structure where the electrode was formed in the at least 1 surface of a charge collector, the purpose of this invention is to provide the manufacturing installation of the lithium ion secondary battery which can improve the pack density of the active material in an electrode.

[0007]

In the lithium ion secondary battery of the structure where the electrode was formed in the at least 1 surface of a charge collector as for the purpose of this invention, it is providing the manufacturing method of the lithium ion secondary battery which can improve the pack density of an electrode active material, and is providing the lithium ion secondary battery which improved the pack density of the electrode active material.

[8000]

[Means for Solving the Problem]

A pressure vessel for this invention for attaining the above-mentioned purpose to lay in an inside a charge collector in which electrode material before a polymerization was applied, it is a manufacturing installation of a lithium ion secondary battery having a force means for pressurizing inside of said pressure vessel at specified pressure, and an energy supply means to supply energy required since electrode material before said polymerization polymerizes within said pressure vessel of said specified pressure.

[0009]

A stage where this invention lays a charge collector in which electrode material before a polymerization was applied in a pressure vessel, It is a manufacturing method of a lithium ion secondary battery having a stage which supplies energy required since electrode material before said polymerization polymerizes within a stage which pressurizes inside of said pressure vessel at specified pressure, and said pressure vessel pressurized by said specified pressure.

A stage where this invention applies a positive pole substance before a polymerization to the 1st field of a charge collector, A stage of laying said charge collector in which a positive pole substance before said polymerization was applied in a pressure vessel, A stage which supplies energy required since a positive pole substance before said polymerization polymerizes within a stage which pressurizes inside of said pressure vessel at specified pressure, and said pressure vessel pressurized by said specified pressure, A stage which applies a negative-electrode substance before a polymerization to the 2nd field of said charge collector, and a stage of laying said charge collector in which a negative-electrode substance before said polymerization was applied in said pressure vessel, It is a manufacturing method of a lithium ion secondary battery having a stage which supplies energy required since a negative-electrode substance before said polymerization polymerizes within a stage which pressurizes inside of said pressure vessel at specified pressure, and said pressure vessel pressurized by said specified pressure.

[00,1]

This invention is a lithium ion secondary battery laminating two or more charge collectors on both sides of an electrolyte between electrodes manufactured by a manufacturing method of said lithium ion secondary battery.

[0012]

This invention is a cell group connecting two or more said lithium ion secondary batteries in parallel and/or in series.

[0013]

This invention is a car using said cell group as a power supply of a motor for driving a wheel. [0014]

[Effect of the Invention]

According to the manufacturing installation of the lithium ion secondary battery of this invention, the lithium ion secondary battery which raised the pack density of the electrode active material can be manufactured.

[0015]

According to the manufacturing method of the lithium ion secondary battery of this invention, the pack density of the electrode active material of a lithium ion secondary battery can be raised. 100161

Since the pack density of the electrode active material of a lithium ion secondary battery was raised according to the lithium ion secondary battery of this invention, the volume energy density, the volume power density, weight energy density, and weight power density of a cell can be improved.

[0017]

Since it was considered as the cell group with the lithium ion secondary battery which raised the pack density of the electrode active material according to the cell group of this invention, the weight and volume of the whole cell group required in order to take out the same energy can be lessened, and high capacity and a high-output battery module can be provided.

[0018]

Since the cell group using the lithlum ion secondary battery which raised the pack density of the electrode active material was used as a power supply for motor drives according to the car of this invention, a higher-output car can be provided.

[0019]

[Embodiment of the Invention]

(A 1st embodiment)

Hereafter, a 1st embodiment of this invention is described with reference to Drawings. [0020]

First, the manufacturing installation of the lithium ion secondary battery cell concerning this invention and the manufacturing method using this are explained.

[0021]

<u>Drawing 1</u> is an explanatory view for explaining the manufacturing installation of the lithium ion secondary battery by this invention, and drawing 2 - 4 are the Drawings for explaining the

manufacturing method of the inhium ion secondary battery by this invention.

The gas bomb 3 containing gas for this manufacturing installation 1 to pressurize the inside of the pressure vessel 2 and the pressure vessel 2, The valve 4 which the gas from the gas bomb 3 is drawn in the pressure vessel 2, and adjusts the pressure in the pressure vessel 2, the pressure release valve 5 for opening the gas in the pressure vessel 2, the heater 6 which heats the inside of the pressure vessel 2, and **, ** and others

[0023]

The pressure vessel 2 can bear a pressure (specified pressure is called hereafter) required in order to enforce the manufacturing method by this invention, and has the inner capacity for putting in the charge collector (detailed after-mentioned) which applied the electrode material before a polymerization to the inside.

[0024]

The gas bomb 3 is a force means and is filled up with the gas for pressurizing the inside of the pressure vessel 2 to specified pressure. A booster pump other than the gas bomb 3 is provided further, and it may be made to pressurize the inside of the pressure vessel 2. By doing in this way, only with the gas pressure from the gas bomb 3, also when the pressure in the pressure vessel 2 is not made to specified pressure, it can respond. In this case, the gas bomb 3 and a booster pump serve as a force means.

[0025]

The gas used for application of pressure does not react in the case of the polymerization of electrode material, and inactive gas, such as helium, argon, and a xenon, or nitrogen gas should be just preferred for it.

[0026]

The valve 4 is adjusted so that it may become specified pressure from the gas bomb 3 about the pressure in the pressure vessel 2 by adjusting with opening and closing of this valve 4 the gas volume supplied in the pressure vessel 2. When a booster pump is provided, the pressure in the pressure vessel 2 may be adjusted with a booster pump.

[0027]

The pressure release valve 5 functions also as a safety valve for extracting the gas in the pressure vessel 2, also when it becomes more than the pressure at which it is a valve for extracting the gas in the pressure vessel 2, and the inside of the pressure vessel 2 was appointed beforehand. A safety valve may be provided independently [the pressure release valve 5]. [0028]

The heater 6 (heating apparatus) is heated to a temperature required in order to polymerize the electrode material before the polymerization which applied the inside of the pressure vessel 2 to the charge collector. Therefore, this heater 6 serves as an energy supply means.

[0029]

As an energy supply means, besides such a heater 6, For example, the ultrasonic irradiation apparatus which irradiates the electrode goods before a polymerization with an ultrasonic wave,

the black light which irradiates the electrode goods before a polymerization with ultraviolet rays, etc. just supply energy required in order to polymerize the electrode material before a polymerization.

[0030]

Next, the manufacturing method of the lithium ion secondary battery which uses this manufacturing installation 1 is explained.

[0031]

Here, manufacture of the cell (a bipolar battery is called) which has the bipolar electrode which formed the anode and the negative electrode in both sides of one charge collector, respectively as a lithium ion secondary battery is explained to an example.

[0032]

The anode and the negative electrode are formed in both sides of one charge collector, and by laminating on both sides of an electrolyte between the anode of this charge collector, and a negative electrode, a bipolar battery constitutes the cell by the anode, the electrolyte, and a negative electrode, and has the structure where the plural laminates of this cell were carried out. [0033]

The manufacturing method in this invention of this bipolar battery manufactures the slurry (the thing before this polymerization is hereafter called an anode slurry) before the polymerization which serves as positive active material formed in a charge collector first, and the slurry (the thing before this polymerization is hereafter called a negative-electrode slurry) before the polymerization used as negative electrode active material.

And as shown in drawing 2, the anode slurry 11 is applied to one side of the charge collector 10.

[0034]

As shown in <u>drawing 1</u>, the charge collector 10 which applied this anode slurry 11, After laying in the pressure vessel 2 and pressurizing the pressure in the pressure vessel 2 to specified pressure, it heats with the heater 6, the anode slurry 11 is polymerized, positive active material is formed in one side of the charge collector 10, and this is made into anode 11' (refer to <u>drawing 3 or drawing 4</u>). Although the number of sheets of the charge collector 10 laid in the pressure vessel 2 considers it as two or more sheets according to the capacity in the pressure vessel 2, the number of sheets is suitably adjusted according to the interior volume of the pressure vessel 2.

[0035]

When pressurizing the inside of the pressure vessel 2, specified pressure is set to 0.5 - 10MPa, for example. Since the electrode before a polymerization is not fully compressed in the case of less than 0.5 MPa and the pack density of this of an electrode active material does not improve, it is not preferred. On the other hand, if 10MPa is exceeded, since the polymerization of the electrolyte contained in a slurry does not advance good, but it becomes insufficient electrolytic polymerizing it and the reactivity of an electrode falls, it is not desirable.

[0036]

On the other hand, temperature is a temperature to which the anode slurry 11 fully polymerizes in the above-mentioned pressure range. Therefore, since it changes "ith substances used as the http://www4.ipdl.inpit.go.jp/cgi-bin/tran web cgi eije?atw u=http%3A%2F%2Fwww4.ipdl.inp... 8/2/2010

anode slurry 11, according to the substance of the anode slurry 11, it adjusts suitably. [0037]

Thus, as the charge collector 10 which formed anode 11' in the whole surface which is the charge collector 10 is taken out from the inside of the pressure vessel 2, then it is shown in <u>drawing 3</u>, the negative-electrode slurry 12 is applied to the field which does not form anode 11' of the charge collector 10 in which this anode 11 was formed.

[0038]

And the charge collector 10 which applied the negative-electrode slurry 12 and which has been anode formed is similarly laid in the pressure vessel 2 with having been shown in <u>drawing 1</u>, After pressurizing the pressure in the pressure vessel 2 to a predetermined pressure, it heats with the heater 6, the negative-electrode slurry 12 is polymerized, negative electrode active material is formed in one side of the charge collector 10, and this is made into negative-electrode 12' (refer to drawing 4).

[0039]

Specified pressure in the pressure vessel 2 at this time as well as the time of the above-mentioned anode formation is set to 0.5 - 10MPa, for example. The Reason made into this pressure range is also depended on the same Reason as the time of the above-mentioned anode formation. Also about temperature, in the above-mentioned pressure range, it is the temperature to which the negative-electrode slurry 12 fully polymerizes, and since it changes with substances made into the negative-electrode slurry 12, according to the substance of the negative-electrode slurry 12, it adiusts suitably.

[0040]

Thus, the anode slurry 11 and the negative-electrode slurry 12 are polymerized in each, putting a pressure, and the high electrode of each active material pack density can be formed on the charge collector 10 by forming anode 11' and negative-electrode 12', respectively.

[0041]

The battery element 15 of a bipolar battery is completed by laminating after that, the charge collector 10 which formed anode 11' and negative-electrode 12' as mentioned above on both sides of the electrolyte 13, as shown in drawing 4. End charge collector 10' of a battery element is formed by the method which mentioned only the anode or the negative electrode above according to each position.

[0042]

And this battery element 15 is completed as the bipolar battery 20 by attaching and carrying out the laminated pack of the electrode tabs 23 and 24 to end charge collector 10', for example, as shown in drawing 5.

[0043]

The members forming of the bipolar battery which can be manufactured below using the manufacturing method by this invention is explained individually.

[0044]

[Charge collector]

a charge collector -- thin-film-fabrication art, such as a process top and a spray coat, -- **** -- film production lamination being carried out, and it being able to form also in what has shape [like], and also [required]. For example, metal powder, such as aluminum, copper, titanium, nickel, stainless steel (SUS), and these alloys, is used as the main ingredients, It heats and comes to fabricate the charge collector metal paste which contains a binder (resin) and a solvent in this, and comes to be formed with the above-mentioned metal powder and a binder. These metal powder may be used for such a charge collector by an one-sort independent, and two or more sorts may be mixed and it may be used for it. That from which the kind of metal powder differs taking advantage of the feature on a process may be laminated to a multilayer. The charge collector which uses aluminum as the above-mentioned metal powder from viewpoints of corrosion resistance, the ease of making, economical efficiency, etc. is preferred.

[0045]

Especially as the above-mentioned binder, it should not be restricted, and conventionally publicly known resin binder materials, such as an epoxy resin, can be used, and also a conductive polymer may be used, for example.

[0046]

As a charge collector, the foil of the above-mentioned metal other than the thing which it comes to form with above metal powder and binders can also be used.

[0047]

Although the thickness in particular of these charge collectors is not limited, it is usually about 1100 micrometers. It is also easy to form taking advantage of the feature on a process, so that the
upper surface and the side peripheral part of an electrode (an anode or a negative electrode) may
also be covered, it is not necessary to call it at a part also from a function and a performance side,
and the shape of a charge collector does not always have to make it approximately regulated
thickness.

[0048]

[Anode (positive active material layer)]

An anode contains positive active material. In addition, in order to improve ion conductivity, an electrolyte, lithium salt, an electric conduction auxiliary agent, etc. may be contained. Although it is desirable especially the electrolyte and to contain the solid polymer electrolyte in either [at least] an anode or a negative electrode preferably, in order to raise the battery characteristic of a bipolar battery more, being contained to both sides is preferred.

[0049]

As the above-mentioned positive active material, the multiple oxide of the transition metal and lithium in which the lithium ion battery of a solution system is also used can be used. Specifically, Li-Fe system multiple oxides, such as Li-min system multiple oxides, such as Li-nickel system multiple oxides, such as Li-Co system multiple oxides, such as LiOOO2, and LiNiO2, and spinel

 ${\rm LiMn_2O_4}$, and ${\rm LiFeO_2}$, etc. are mentioned. In addition, the phosphoric acid compound and sulfated compound; ${\rm V_2O_5}$ of transition metals, such as ${\rm LiFePO_4}$, and lithium, Transition metal oxides and

sulfides, such as MnO₂, TiS₂, MoS₂, and MoO₃;P bO₂, AgO, NiOOH, etc. are mentioned.

On a process, the particle diameter of positive active material is pasted in the state before polymerizing a positive electrode material, is applied by a spray coat etc., and just forms membranes.

[0051]

The loadings of the positive active material in an anode, an electrolyte (preferably solid polymer electrolyte), lithium salt, and an electric conduction auxiliary agent should be determined in consideration of the purposes of using a cell (output serious consideration, energy serious consideration, etc.), and ion conductivity. For example, if there are too few loadings of the electrolyte in an anode, especially a solid polymer electrolyte, ion conduction resistance and ionic diffusion resistance within an active material layer will become large, and battery capacity will fall. On the other hand, if there are too many loadings of the electrolyte in an anode, especially a solid polymer electrolyte, the energy density of a cell will fall. Therefore, in consideration of these factors, the amount of solid polymer electrolytes corresponding to the purpose is determined. [0052]

The case where the bipolar battery which gives priority to cell reaction nature here using the solid polymer electrolyte (ionic conductivity: 10^{-5} - 10^{-4} S/cm) of an actual condition level is manufactured is considered concretely. ** -- in order to obtain the bipolar battery which has the feature [like], an electric conduction auxiliary agent is made more, or bulk density of an active material is lowered, and the electronic conduction resistance between active material particles is maintained lowness. A cavity part is increased simultaneously and this cavity part is filled up with a solid polymer electrolyte. ** -- it is good for processing [like] to raise the rate of a solid polymer electrolyte. [10053]

The thickness in particular of an anode should not be limited, and as loadings were described, it should be determined in consideration of the purposes of using a cell (output serious consideration, energy serious consideration, etc.), and ion conductivity. The thickness of a general positive active material layer is about 10-500 micrometers.

[0054]

[Negative electrode (negative electrode active material layer)]

A negative electrode contains negative electrode active material. Like an anode, in order to improve ion conductivity, an electrolyte, lithium salt, an electric conduction auxiliary agent, etc. may be contained. Except the kind of negative electrode active material, since it is the same as that of the contents fundamentally indicated by the paragraph of the [anode], explanation is omitted here. 100551

As negative electrode active material, the negative electrode active material in which the lithium ion battery of a solution system is also used can be used. However, since a solid polymer electrolyte is used [a bipolar battery] suitably, when the reactivity in this solid polymer electrolyte is taken into consideration, a metallic oxide, lithium metal multiple oxide metal, carbon, etc. are

preferred. They are carbon, a transition metal oxide, and a lithium transition metal multiple oxide more preferably. They are titanium oxide, a lithium titanium multiple oxide, and carbon still more preferably. These may be used by an one-sort independent and may use two or more sorts together.

[0056] [Electrolyte]

[0057]

It can use, if liquid junction can be prevented as an electrolyte even if it is a solid polymer electrolyte or a polymer gel electrolyte. These can also be used together. An electrolyte can also be made into multilayer structure and the layer which changed an electrolytic kind and ingredient compounding ratio by the anode and negative-electrode side can also be formed.

When using a polymer gel electrolyte, the ratios (mass ratio) of polymer and the electrolysis solution which constitute this polymer gel electrolyte are 20:80-95:5, and a range with a comparatively small ratio of an electrolysis solution, but it is a solid polymer electrolyte more preferably. A solid polymer electrolyte excels [this] in heat resistance as compared with a polymer gel electrolyte or a liquid electrolyte, It is because the characteristic peculiar to the solid polymer electrolyte that there is no possibility of carrying out a pyrolysis, gasifying at an elevated temperature, or igniting, and ****, excel in tolerance, are hard to produce the liquid leakage and the short circuit by breakage in external load etc., it is still compacter, and shape is made freely can be

[0058]

used effectively.

The above-mentioned solid polymer electrolyte is a layer which comprises Polymer Division which has ion conductivity, and material will not be limited if ion conductivity is shown. As a solid polymer electrolyte, polyethylene oxide (PEO), polypropylene oxide (PPO), and a publicly known solid polymer electrolyte like these copolymers are mentioned. In a solid polymer electrolyte, in order to secure ion conductivity, lithium salt is contained. As lithium salt, LiBF₄, LiPF₆, LiN(SO₂CF₃) ₂, LiN

 $(SO_2C_2F_5)_{2'}$ or these mixtures can be used. However, it is not necessarily restricted to these.

Polyalkylene oxide system Polymer Division like PEOPPO may dissolve well lithium salt, such as $LiBF_4$, $LiPF_6$, $LiN(SO_2CF_3)_2$, and $LiN(SO_2C_2F_5)_2$. The outstanding mechanical strength is revealed by forming the structure of cross linkage.

[0059]

Although a polymer gel electrolyte contains the electrolysis solution usually used for the solid polymer electrolyte which has ion conductivity with a lithium ion battery, the thing which made the same electrolysis solution hold is also further contained in the skeleton of Polymer Division without lithium ion conductivity.

[0060]

Here, the difference between a solid polymer electrolyte and a polymer gel electrolyte is specified as follows.

[0061]

The thing having contained the electrolysis solution usually used for solid polymer electrolytes, such as polyethylene oxide (PEO), with a lithium ion battery is a polymer gel electrolyte. [0062]

The thing which made the electrolysis solution hold in the skeleton of Polymer Division without lithium ion conductivity, such as polyvinylidene fluoride (PVDF), also hits a polymer gel electrolyte. [0063]

If the ratio of the polymer which constitutes a polymer gel electrolyte, and an electrolysis solution is broad, and polymer (Polymer Division) 100% is used as a solid polymer electrolyte and it uses 100% of an electrolysis solution as a liquid electrolyte, all the intermediates will hit a polymer gel electrolyte.

[0064]

The above-mentioned solid polymer electrolyte will not be limited in particular, if it is Polymer Division which has ion conductivity. As Polymer Division which has ion conductivity, polyalkylene oxide system Polymer Division, such as polyethylene oxide (PEO) and polypropylene oxide (PPO), these copolymers, etc. are mentioned. Poly which is a copolymer of what has in a copolymer the Polymer Division chain which has ion conductivity at least, and should not just have ionic conduction nature like polyvinylidene fluoride (it may be fluoridation vinylidene-hexafluoropropylene etc.) Above-mentioned polyalkylene oxide system Polymer Division may dissolve well lithium salt, such as LiBF₄, LiPF₆, LiN(SO₂CF₃)₂, and LiN(SO₂C₂F₆)₂. It is advantageous by forming the structure of cross linkage at the point which the outstanding mechanical strength reveals.

[0065]

The above-mentioned polymer gel electrolyte contains the electrolysis solution usually used for the solid polymer electrolyte which has ion conductivity with a lithium ion battery, as specified above, but. The thing which made the same electrolysis solution hold is also contained in the skeleton of Polymer Division without lithium ion conductivity.

[0066] Here as an electrolysis solution (electrolyte salt and plasticizer) contained in a polymer gel electrolyte, Usually, that what is necessary is just what is used with a lithium ion battery. For example, LiPF $_6$, LiBF $_4$, LiClO $_4$, LiAsF $_6$, LiTaF $_6$, LiAlCl $_4$, Inorganic acid anionic salt, such as Li $_2$ B $_{10}$ Cl $_{10}$, LiCF $_3$ SO $_3$, . Are chosen from organic acid anionic salt, such as Li(CF $_3$ SO $_2$) $_2$ N Including at least one kind of lithium salt (electrolyte salt), propylene carbonate, Cyclic carbonate, such as ethylene carbonate; Dimethyl carbonate, Chain carbonate, such as methylethyl carbonate and diethyl carbonate; A tetrahydrofuran, 2-methyltetrahydrofuran, 1,4-dioxane, 1, 2-dimethoxyethane, ether [, such as 1,2-dibutoxyethane,]; -- lactone [, such as gamma-butyrolactone]; -- nitril [, such as acetonitrile]; -- ester species [, such as methyl

propionate]; -- amide [, such as dimethylformamide]; -- methyl acetate. The thing using organic

being chosen from methyl formate as it is few can be used. However, it is not necessarily restricted to these.

[0067]

As Polymer Division without the lithium ion conductivity used for a polymer gel electrolyte, polyvinylidene fluoride (PVDF), polyvinyl chloride (PVC), polyacrylonitrile (PAN), polymethylmethacrylate (PMMA), etc. can be used, for example. However, it is not necessarily restricted to these. Since it is a thing included in the category which does not rather almost have ion conductivity, it can also be considered as Polymer Division which has the above-mentioned ion conductivity, but PAN, PMMA, etc. are illustrated as Polymer Division without the lithium ion conductivity used for a polymer gel electrolyte here.

As the above-mentioned lithium salt, for example LiPF₆, LiBF₄, LiClO₄, LiAsF₆, LiTaF₆, Organic acid anionic salt, such as inorganic acid anionic salt, such as LiAlCl₄ and Li₂B₁₀Cl₁₀, Li(CF₃SO₂) ₂N, and Li(C₂F₅SO₂) ₂N, or these mixtures can be used. However, it is not necessarily restricted to these.

[0069]

[0068]

Acetylene black, carbon black, graphite, etc. are mentioned as an electric conduction auxiliary agent. However, it is not necessarily restricted to these.

[0070]

These solid polymer electrolytes or a polymer gel electrolyte may be contained also in an anode and/or a negative electrode as everything but the polymer electrolyte which constitutes a cell was described above, but. The polymer electrolyte which changes with the polymer electrolytes, anodes, and negative electrodes which constitute a cell may be used, the same polymer electrolyte may be used and the polymer electrolyte which changes with layers may be used. 100711

Electrolytic thickness in particular is not limited. However, in order to obtain a compact bipolar battery, it is preferred to make it thin as much as possible in the range which can secure the function as an electrolyte. The thickness of a general solid polymer electrolyte layer is about 10-100 micrometers. It is also easy to form taking advantage of the feature on a process, so that the upper surface and the side peripheral part of an electrode (an anode or a negative electrode) may also be covered, it is not necessary to call it at a part also from a function and a performance side, and the electrolytic shape does not always have to make it approximately regulated thickness. [0072]

By the way, in this embodiment, Polymer Division for solid polymer electrolytes used preferably is polyether system Polymer Division like PEO and PPO. For this reason, the oxidation resistance by the side of the anode under high temperature service is weak. Therefore, when using an anode agent with a high oxidation-reduction potential generally used with the lithium ion battery of a solution system, few things are more preferred than the capacity of the anode in which the capacity of a negative electrode counters via a solid polymer electrolyte. Anode potential can be prevented

from going up too much at a charging end term if less than the capacity of the anode in which the capacity of a negative electrode counters. The capacity of an anode and a negative electrode can be calculated from manufacturing conditions as theoretical capacity at the time of manufacturing an anode and a negative electrode. The capacity of a finished product may be measured directly with a measuring device.

[0073]

However, since there is a possibility that negative-electrode potential may fall too much and the endurance of a cell may be spoiled when small compared with the capacity of the anode in which the capacity of a negative electrode counters, it needs to be cautious of charge and discharge voltage. For example, it is set as a suitable value to the oxidation-reduction potential of the positive active material which uses the average charge voltages of the cell of 1, and warns against endurance falling.

[0074]

[Insulating layer]

An insulating layer (un-illustrating) is the purpose of preventing the short circuit by irregular ** with a slight end of a laminated electrode from charge collectors contacting, or an electrolysis solution beginning to leak, or taking place, and it comes to form it in the circumference of each electrode. [0075]

As this insulating layer, by thin-film-fabrication art, such as a spray coat, on a process. **** -- it is what is produced also to what has shape [like] and can be formed -- and insulation. Although what is necessary is to have the sealing nature (sealing performance) over a break through of an electrolyte or the moisture permeation of the moisture from the outside, the heat resistance under battery operation temperature, etc., and just to be able to use an epoxy resin, rubber, polyethylene, polypropylene, etc., From viewpoints of corrosion resistance, chemical resistance, the ease (film production nature) of making, economical efficiency, etc., an epoxy resin is preferred.

[0076]

[A positive electrode tab and a negative electrode tab]

About a positive electrode tab and a negative electrode tab, the publicly known electrode tab usually used with a lithium ion battery can be used.

[0077]

[Battery armor material (cell case)]

In order that a bipolar battery may prevent the shock from the outside at the time of using it, and environmental degradation, the battery element is accommodated in battery armor material thru/or a cell case. A Polymer Division-metal compound laminate film, an aluminum laminated pack, etc. which covered metal (an alloy is included), such as aluminum, stainless steel, nickel, and copper, with insulators, such as a polypropylene film, from a viewpoint of a weight saving, It is preferred by joining a part or all of the periphery by thermal melting arrival using publicly known battery armor material conventionally to have composition which stored and sealed the cell layered product. In this case, what is necessary is just to let the above-mentioned anode and a negative electrode tab be the structures which are inserted into the above-mentioned heat sealed part, and are exposed

to the exterior of the above-mentioned battery armor material. As shown in <u>drawing 5</u>, it is preferred to use the Polymer Division-metal compound laminate film excellent in thermal conductivity, an aluminum laminated pack, etc. at the point that heat can be efficiently told from the heat source of a car, and the inside of a cell can be quickly heated to battery operation temperature.

[0078]

<The example of an experiment>

The bipolar battery by a 1st embodiment constituted as mentioned above was actually manufactured, and the charge and discharge test was done.

[0079]

[Manufacture of a sample cell]

(Anode formation)

As positive active material, as LiMn₂O₄ (41.7%) and an electric conduction adjuvant Acetylene black (8.3%), As polymer, the copolymer of polyethylene oxide (PEO) and polypropylene oxide (PPO) (33.3%), NMP (optimum dose) was mixed as Li(C₂F₅SO₂) ₂N (16.7%) and a slurry viscosity material adjustment solvent as a supporting electrolyte, azobisuisobutironitoriru (it is 1000 ppm to the amount of polymer) was mixed as a polymerization initiator, and the anode slurry was adjusted.

100801

It applied to one side of the stainless steel foil of 20-micrometer thickness using the abovementioned anode slurry as a charge collector, this was laid in the pressure vessel 2 of the manufacturing installation 1 by this invention, the inside of the pressure vessel 2 was purged with argon gas, and the inside of the pressure vessel 2 was further pressurized to 1MPa with argon gas.

[0081]

Then, the inside of the pressure vessel 2 was heated to 110 ** with the heater 6, and this temperature was maintained for 5 hours.

[0082]

The anode slurry polymerized by this and it became an anode. The thickness of the done anode was 40 micrometers.

[0083]

(Negative-electrode formation)

As negative electrode active material, as LiTi5O12 (28.1%) and an electric conduction adjuvant Acetylene black (8.4%), As polymer, the copolymer of polyethylene oxide (PEO) and polypropylene oxide (PPO) (42.1%), NMP (optimum dose) was mixed as $\text{Li}(C_5F_8\text{SO}_2)_2\text{N}$ (21.3%) and a slurry

viscosity material adjustment solvent as a supporting electrolyte, azobisuisobutironitoriru (it is 1000 ppm to the amount of polymer) was mixed as a polymerization initiator, and the negative-electrode slurry was adjusted.

[0084]

The above-mentioned anode applies the above-mentioned negative-electrode slurry to the field in which the anode of the charge collector (stainless steel foil of 20-micrometer thickness) already formed in one side is not formed, and this is laid in the pressure vessel 2 of the manufacturing installation 1 by this invention, The inside of the pressure vessel 2 was purged with argon gas, and the inside of the pressure vessel 2 was further pressurized to 1MPa with argon gas. [0085]

Then, the inside of the pressure vessel 2 was heated to 110 ** with the heater 6, and this temperature was maintained for 5 hours.

[0086]

The negative-electrode slurry polymerized by this and it became a negative electrode. The thickness of the done negative electrode was 40 micrometers.

[0087]

[8800]

The bipolar electrode in which the anode and the negative electrode were formed in both sides of the charge collector of one sheet by this, respectively was done.

(Cell manufacture)

Using the bipolar electrode formed as mentioned above, apply 50 micrometers to an anode and a 50-micrometer electrolyte is applied to a negative electrode, respectively, As it was crowded with the anode and the negative electrode on both sides of this electrolyte, the cell was constituted (therefore, electrolytic thickness is 100 micrometers), the charge collector was laminated so that this cell might be five layers, and the battery element was manufactured. The number of mols [O] of the oxygen atom in which polymer has the used electrolyte in the copolymer of polyethylene oxide (PEO) and polypropylene oxide (PPO), The number of mols of the lithium ion which is dissolving into an electrolyte [Li] is the solid polymer electrolyte in which Li($C_2F_5SO_2$) $_2N$ was

dissolved so that it may become a ratio called [O]/[Li]=16.

100891

What formed only the anode in one side of a charge collector, and the thing in which only the negative electrode was formed are used only for the end charge collector of a battery element by the method mentioned above, respectively.

[0090]

The laminated pack of the electrode tab was attached and carried out to the end charge collector of the battery element manufactured as mentioned above, and it was considered as the bipolar battery. This bipolar battery is called working example.

[0091]

The bipolar battery using the electrode which polymerized the anode slurry and the negativeelectrode slurry only with heating under atmospheric pressure was also manufactured without pressurizing in formation of an anode and a negative electrode for comparison. This bipolar battery is called a comparative example.

100921

[Evaluation]

The charge and discharge test was done. The examination charged each cell of working example and a comparative example to 21V, and it discharged until it was set to 12.5V by 0.1CA. [0093]

The service capacity per anode unit volume was 75 mAh/cm³ by the cell of working example which applied this invention as a result of the examination. On the other hand, in the cell of a comparative example using the electrode which is not pressurized, it was 43 mAh/cm³.

[0094]

In the cell using the electrode polymerized while pressurizing so that the result of this charge and discharge test may show, charge-and-discharge capacity per unit volume can be made high. When the pack density of an electrode active material improves, contact of active material particles becomes good, the internal resistance of an electrode decreases, and an output improves. [0095]

As explained above, according to a 1st embodiment that applied this invention, by polymerizing a bipolar electrode under application of pressure, and forming, it can become possible to raise the pack density of an electrode active material, and the output per unit volume of an electrode can be raised.

100961

(A 2nd embodiment)

A 2nd embodiment is the cell group which connected two or more bipolar batteries by a 1st embodiment mentioned above.

[0097]

<u>Drawing 6</u> is a perspective view of the cell group by a 3rd embodiment, and <u>drawing 7</u> is the <u>Drawings</u> which looked at the internal configuration from the upper part.

186001

This cell group 50 connects still in parallel what connected to series two or more bipolar batteries 20 (refer to drawing.5) by a 1st embodiment mentioned above so that it may illustrate. The electrodes 23 and 24 of each cell are connected to bipolar battery 20 comrades by the electric conduction bar 53. The electrode terminals 51 and 52 are established in the one side face of the cell group 50 as an electrode of this cell group 50 at this cell group 50.

[0099]

In this cell group, ultrasonic welding, hot welding, laser welding, a rivet, a caulking, an electron beam, etc. can be used as a connection method at the time of connecting the cell 20 directly and connecting still in parallel. By taking such a connection method, a cell group with long-term reliability can be manufactured.

[0100]

By cell-group-izing using the cell by a 1st embodiment mentioned above according to the cell group by a 2nd embodiment, if it is a cell group of the same size, it can obtain with high capacity and high power conventionally.

[0101] Conne

Connection of the bipolar battery 20 as a cell group may connect two or more bipolar batteries 20 to parallel altogether, and may connect two or more bipolar batteries 20 to series altogether. [0102]

(A 3rd embodiment)

A 3rd embodiment is the cell group module which connected two or more cell groups by a 2nd embodiment mentioned above.

[0103]

Drawing 8 is a perspective view of the cell group module by a 3rd embodiment.

[0104]

This cell group module 60 laminates two or more cell groups 50 by a 2nd embodiment mentioned above, and connects and modularizes the electrode terminals 51 and 52 of the class cell 50 with the electric conduction bars 61 and 62.

[0105]

Thus, by modularizing the cell group 50, cell control is made easy, for example, it becomes the cell group module optimal as objects for ****, such as an electromobile and a hybrid car. And since the cell group mentioned above is used for this cell group module 60, it becomes what has high long-term reliability.

[0106]

Such a cell group module is also one sort of a cell group.

[0107]

(A 4th embodiment)

A 4th embodiment is a car which carries the cell group module by a 3rd embodiment mentioned above, and is used as a power supply of a motor. As a car using a cell group module as a power supply for motors, they are cars which are driving the wheel by the motor, such as an electromobile and a hybrid car, for example.

[0108]

By reference, the schematic diagram of the car 100 carrying the cell group module 60 is shown in drawing.2. The cell group module 60 carried in a car has the characteristic which explained [above-mentioned]. For this reason, the car carrying the cell group module 60 has high endurance, and even if it is after using it over a long period of time, it can provide sufficient output. [0109]

Although the embodiment which applied this invention above was described, this invention is not limited to these embodiments. For example, although the embodiment mentioned above explained manufacture of the bipolar battery with bipolar electrode structure to the example, This invention becomes possible [it being suitable also for manufacture of the lithium ion secondary battery of the type which is not limited to manufacture of such a bipolar electrode and has an electrode only in one side of a charge collector, improving the pack density of an electrode, and raising the output]. [Brief Description of the Drawings]

 $[\underline{\text{Drawing 1}}] \textbf{It is an explanatory view for explaining the manufacturing installation of the lithium ion} \\$

secondary battery by this invention.

[Drawing 2]They are the Drawings for explaining the manufacturing method of the lithium ion secondary battery by this invention.

[Drawing 3]They are the Drawings for explaining the manufacturing method of a lithium ion secondary battery following drawing 2.

[Drawing 4]They are the Drawings for explaining the manufacturing method of a lithium ion secondary battery following drawing 3.

[Drawing 5]It is a perspective view showing the appearance of a bipolar battery.

[Drawing 6]It is a perspective view showing the cell group using the above-mentioned bipolar battery.

[Drawing 7]They are the Drawings which looked at the internal configuration of the abovementioned cell group from the upper part.

[Drawing 8]It is a perspective view showing the battery module which connected two or more above-mentioned cell groups.

[<u>Drawing 9</u>]They are Drawings in which the car carrying the above-mentioned battery module is shown.

[Description of Notations]

- 1 Manufacturing installation
- 2 Pressure vessel
- 3 Gas bomb
- 4 Valve
- 5 Pressure release valve
- 6 Heater 10 Charge collector
- 11 Anode slurry
- 11 Anode
- 12 Negative-electrode slurry
- 12 Negative electrode
- 13 Electrolyte
- 15 Battery element
- 20 Bipolar battery
- 23, 24 electrode tabs
- 50 Cell group
- 60 Cell group module
- 100 Car

[Translation done.]